



# Synergistic effect of surface oxygen vacancies and interfacial charge transfer on Fe(III)/Bi<sub>2</sub>MoO<sub>6</sub> for efficient photocatalysis

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## ABSTRACT

Novel Fe(III) clusters grafted Bi<sub>2</sub>MoO<sub>6</sub> nanosheets with surface oxygen vacancies (denoted as F/BMO-SOVs) heterostructured composite have been firstly fabricated via a reliable calcination process combined with impregnation approach. The surface oxygen vacancies (SOVs) in Bi<sub>2</sub>MoO<sub>6</sub> were formed due to controlled calcination process. The presence of Fe (III) clusters was confirmed by HRTEM, XPS, and UV–vis DRS. Under visible light irradiation, the optimum molar ratio of 15% F/BMO-SOVs achieved 93.4% degradation efficiency of phenol within 180 min, representing nearly 80 times higher activity than the pure Bi<sub>2</sub>MoO<sub>6</sub>, confirmed by both absorption spectrum and TOC measurement. The dramatically enhanced photocatalytic activity is attributed to the synergistic effect between the SOVs, Fe(III) clusters and Bi<sub>2</sub>MoO<sub>6</sub>, which not only narrows the band gap, improving the visible light response ability, but also facilitates the direct interfacial charge transfer (IFCT) from the SOVs to the surface Fe(III) clusters, greatly promoting the efficient separation of photogenerated electron-hole pairs. According to the trapping experiments and ESR measurements results, ·O<sub>2</sub><sup>-</sup>, ·OH, and h<sup>+</sup> all participated in the phenol photodegradation process over F/BMO-SOVs. Thus, this work not only provides a synergistic effect between SOVs, Fe(III) clusters and Bi<sub>2</sub>MoO<sub>6</sub> involving an IFCT process, but also proposes an efficient approach to fabricating highly active photocatalysts in environmental remediation and solar fuel synthesis.

## 1. Introduction

Phenol and phenolic compounds in water bodies have been listed as a class of priority pollutants by the United States Environmental Protection Agency (USEPA), because of their persistence and high toxicity, and could cause respiratory, nervous and cardiovascular problems to human beings [1–3]. The World Health Organization (WHO) has also strictly regulated total phenols concentration below 0.5 µg L<sup>-1</sup> for drinking water [2]. Therefore, it is highly desirable to develop effective technologies to further eliminate phenol and phenolic compounds in water.

In consideration of solar energy conversion, semiconductor-based photocatalysis has been viewed as one of the most promising green technology for the removal of phenol and phenolic compounds from aqueous media [4,5]. Among various semiconductor materials, Bi-

based semiconductors such as Bi<sub>2</sub>WO<sub>6</sub> and Bi<sub>2</sub>MoO<sub>6</sub>, belonging to the Aurivillius family, have received considerable scientific research interest due to their layered structures and high catalytic properties [6,7]. In particular, Bi<sub>2</sub>MoO<sub>6</sub> is a photocatalyst with band gap of 2.5–2.8 eV, and is nontoxic, highly photostable, thermally stable and eco-friendly. Recently, Zhu et al. [8] revealed that Bi<sub>2</sub>MoO<sub>6</sub> may be a potential candidate as one of the most promising visible light-driven photocatalyst for degradation of organic pollutants in wastewater. Nonetheless, the overall solar energy conversion efficiency remains limited by visible-light responsive region, the relatively rapid recombination of photoexcited electron-hole pairs and slow carrier transport [9,10]. Hence, it is imperative to explore effective ways to further extend the range of visible-light response and improve the photocatalytic activity of Bi<sub>2</sub>MoO<sub>6</sub>.

The introduction of surface oxygen vacancies (SOVs) is one effective

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approach to narrow the band gap and suppress the recombination of photogenerated charge carriers in semiconductors, in order to achieve high visible-light-driven photocatalytic activity [11]. It has been reported that SOVs with abundant localized electrons are of particular interest for the enhanced adsorption and activation of  $O_2$  to reactive oxygen species, which could further inhibit the recombination of photogenerated charge carriers [12–15]. Recently, many researchers have reported different kinds of semiconductor-based photocatalysts, such as  $TiO_2$ ,  $BiOBr$ , and  $BiVO_4$ , which displayed excellent visible-light photocatalytic activities [16–18]. Zhu et al. [19] reported that the introduction of SOVs in  $BiPO_4$  via a solvothermal-calcination route could broaden the valence band, thus leading to an improved photocatalytic activities. Recently, Huang et al. [20] used a high pressure hydrogenation treatment process to prepare SOVs-rich  $BiFeO_3$  nanocrystals. The presence of SOVs in  $BiFeO_3$  resulted into a narrow band gap and also facilitated the separation of photogenerated electron-hole pairs. A similar phenomenon has also been observed on  $Bi_2O_3$  by Lu's group [21]. However, a study based on  $Bi_2MoO_6$  with SOVs has not been reported.

Besides the introduction of SOVs, the cationic clusters-grafting is another efficient strategy to enhance the visible-light-driven activity of semiconductor photocatalysts via interfacial charge transfer (IFCT) [22]. Currently, the grafting of cationic clusters, such as Cu(II) and Fe(III) clusters on the surface of  $TiO_2$ , which could extend light absorption to the visible light region, and subsequently increase the photocatalytic efficiency have been reported [23–26]. This efficient strategy has also been applied to non- $TiO_2$  semiconductors, to enhance visible light photocatalytic activity [27–29]. For example, Qiu et al. [30] prepared efficient visible-light-driven  $BiOCl$  photocatalysts by grafting Fe(III) clusters on the surface of  $BiOCl$  microflowers through a simple impregnation method. He found that the enhancement in visible-light driven photocatalytic activity of the Fe(III)-grafted  $BiOCl$  photocatalysts was attributed to the fact that the Fe(III) clusters can facilitate the separation of photogenerated electron-hole via IFCT process under visible light irradiation. In addition, Dong et al. [31] reported that the grafting of Fe(III) clusters onto the surface of  $(BiO)_2CO_3$  hierarchical structure, through the impregnation method, can enhance the photocatalytic activity of  $(BiO)_2CO_3$ , originating from the IFCT effect between the Fe(III) clusters and  $(BiO)_2CO_3$ . To the best of our knowledge, the IFCT effect of Fe(III) clusters on the surface of  $Bi_2MoO_6$  for enhancing its photocatalytic activity has not been reported.

To achieve an optimal photocatalytic activity, the combination of above-mentioned two strategies is applied to the preparation of a composite photocatalyst, which can produce a strong synergistic effect for the efficient photodecomposition of contaminants. Herein, we report a novel F/BMO-SOVs photocatalyst that has been rationally designed and successfully fabricated via solvothermal synthesis of  $Bi_2MoO_6$ . The as-prepared  $Bi_2MoO_6$  nanosheets with surface oxygen vacancies (denoted as BMO-SOVs) were impregnated with Fe(III) clusters. The photocatalytic performance of the prepared composites was investigated by degrading a colorless organic model pollutant (phenol) under visible light irradiation. It is shown that the obtained F/BMO-SOVs photocatalyst demonstrated a remarkable enhancement in photocatalytic activity for degradation of phenol as compared with those of  $Bi_2MoO_6$ , BMO-SOVs, and F/BMO under visible light illumination. The highly enhanced photocatalytic efficiency observed in F/BMO-SOVs should be attributed to the synergistic effect of the SOVs and IFCT. The present work has been proven to be a new combined strategy, which is also applicable to the design and construction of other photocatalytic systems to enhance photocatalytic performance.

## 2. Experimental section

### 2.1. Sample preparation

#### 2.1.1. Preparation of $Bi_2MoO_6$ with surface oxygen vacancies (BMO-SOVs)

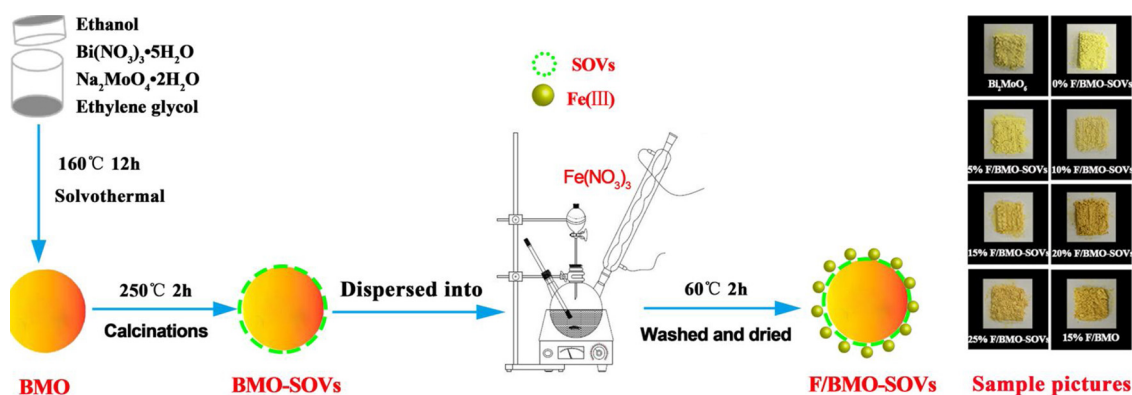
All the chemicals were of analytical grade and used as received. Distilled water was used in all experiments.  $Bi_2MoO_6$  with surface oxygen vacancies was prepared according to a procedure described in our previous work [32]. In a typical process, 1.3 mmol of  $Bi(NO_3)_3 \cdot 5H_2O$  and 0.65 mmol of  $Na_2MoO_4 \cdot 2H_2O$  were dispersed in 13.0 mL of ethylene glycol (EG) under vigorous stirring until a transparent solution was formed. Afterwards, 32.5 mL of ethanol was added and the mixture was stirred for another 30 min. Finally, the mixed solution was transferred into a 65.0 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 160 °C for 12 h. The product was separated by centrifugation and washed with deionized water three times and then dried at 60 °C in a vacuum oven for 12 h. The obtained product was marked as BMO. Subsequently, these products were annealing at 250 °C for 2 h in air with the heating rate of 2 °C/min in order to introduce extra surface oxygen vacancies, and the resulting products were denoted as BMO-SOVs ( $Bi_2MoO_6$  with surface oxygen vacancies).

#### 2.1.2. Synthesis of Fe(III)/ $Bi_2MoO_6$ -SOVs (F/BMO-SOVs) photocatalysts

The Fe(III)/ $Bi_2MoO_6$ -SOVs photocatalyst was prepared by an impregnation technique as reported previously [31]. Specifically, 0.305 g of BMO-SOVs sample was uniformly dispersed in 50 mL distilled water via ultrasonic treatment for 30 min. The aqueous suspension was transferred into a thermostat water bath at 60 °C and stirred for 20 min. Afterwards, varying amounts of  $Fe(NO_3)_3$  aqueous solution was slowly added into the above solution, followed by stirring at 60 °C for 2 h. The final product was filtered, washed several times with deionized water and ethanol, and dried at 60 °C for 12 h in a vacuum oven. The theoretical molar ratio of  $Fe(NO_3)_3$  to BMO-SOVs was controlled at 5%, 10%, 15%, 20%, and 25%, respectively. Accordingly, the resultant product was milled into powder and labeled as 5% F/BMO-SOVs, 10% F/BMO-SOVs, 15% F/BMO-SOVs, 20% F/BMO-SOVs, and 25% F/BMO-SOVs. For comparison, 15% Fe(III)/ $Bi_2MoO_6$  was synthesized by the same procedure, but replacing BMO-SOVs with  $Bi_2MoO_6$ , and the obtained product was labeled as 15% F/BMO. The preparation process of F/BMO-SOVs composite is shown in Scheme 1.

### 2.2. Characterization of photocatalysts

Powder X-ray diffraction (XRD) was carried out on a Shimadzu XRD-7000 X-ray diffractometer using  $Cu K\alpha$  radiation ( $\lambda = 0.15418$  nm) at a scanning rate of  $2^\circ \text{ min}^{-1}$  in a  $2\theta$  range of  $5^\circ - 80^\circ$ . The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5400 X-ray photoelectron spectrometer. Field emission scanning electron microscope (FE-SEM) images were recorded on a JSM-6700 F scanning electron microscope. Energy-dispersive X-ray (EDS) spectra were obtained using a JEOL-2100 at an accelerating voltage of 200 kV. High-resolution transmission electron microscope (HRTEM) images was recorded on a JEM-2100 electron microscope operated at an accelerating voltage of 200 kV. In situ electron paramagnetic resonance (EPR) measurement was taken in an endor spectrometer (JEOL ES-ED3X). The g factor was obtained by taking the signal of manganese as standard. The electron spin resonance (ESR) signals of radicals, trapped by a spin-trap reagent DMPO (5,5'-dimethyl-1-pyrroline-N-oxide) (Sigma Chemical Co.) in water, were examined on a Bruker model ESR JES-FA200 spectrometer equipped with a Quanta-Ray Nd: YAG laser system as the irradiation source ( $\lambda \geq 420$  nm). To minimize experimental errors, the same type of quartz capillary tube was used for all ESR measurements. Raman spectra were recorded by using a Horiba Jobin-Yvon LabRam HR800 Raman microspectrometer,



Scheme 1. Schematic illustration of the preparation process of F/BMO-SOVs samples.

with laser excitation at 320 nm. The UV–vis diffuse reflectance spectra (UV–vis-DRS) of the samples were obtained using Shimadzu UV-2550 UV–vis spectrophotometer. BaSO<sub>4</sub> was used as a reflectance standard. Room-temperature photoluminescence spectra (PL) and time-resolved photoluminescence spectra (TR-PL) were detected with a Horiba FLTCSPC fluorescence spectrophotometer. Photoelectrochemical properties such as photocurrent (PC) and electrochemical impedance spectra (EIS) were performed on an electrochemical analyzer (CHI660D, CHI Shanghai, Inc.) in a standard three-electrode configuration with a Platinum wire as the counter electrode and saturated calomel electrodes (in saturated KCl) as a reference electrode [32].

### 2.3. Photocatalytic activity

Evaluation of the photocatalytic activities of as-prepared samples towards complete degradation of the colorless organic model pollutant (phenol) was performed as follows: A 400 W halogen lamp (Nanjing XuJiang electrical and mechanical plant, Nanjing, P. R. China) with a 420 nm cut-off filter was chosen as the visible light source. A suspension containing 200 mg of photocatalyst and 200 mL of 10 mg L<sup>-1</sup> phenol (1.0 g<sub>cat</sub>/L<sub>solution</sub>) fresh aqueous solution were continuously stirred in the dark for 30 min to establish an adsorption/desorption equilibrium of phenol solution. After this period of time, the light source was turned on. During the reaction, a 5.0 mL sample was withdrawn at given time intervals and the photocatalysts were then separated by centrifugation. The residual concentration of phenol in solution was estimated using absorption at 507 nm by a Shimadzu 2550 UV–vis spectrophotometer following the 4-aminoantipyrine colorimetric method [33]. Total organic carbon (TOC) in the phenol solution was recorded by automatic total organic carbon analyzer (VARIO, Elementar, Germany).

### 2.4. Computational details

First-principles calculations have been performed with density functional theory (DFT) as implemented in Vienna *ab initio* simulation package (VASP) [34]. The Perdew-Burke-Ernzerhof (PBE) approach was adopted to describe the exchange correlation effects on the basis of the Projected Augmented Wave (PAW) method with plane wave cutoff energy of 450 eV [35]. During geometry optimization, all of the structures were relaxed until the component of force acting on each atom was smaller than  $1 \times 10^{-2}$  eV/Å, and the convergence of the total energy was close to  $1 \times 10^{-5}$  eV/cell.

The Bi<sub>2</sub>MoO<sub>6</sub> of space group Pca2<sub>1</sub> was selected as computational model according to XRD. The Monkhorst-Pack Method [36] with k-points grids of  $6 \times 6 \times 2$  was used for describing the Brillouin zone corresponding to supercell ( $2 \times 1 \times 2$  unit cell). The oxygen defect formation energy was defined as:

$$E_{\text{form}} = E_{\text{Bi8Mo4O23}} + \mu_{\text{O}} - E_{\text{Bi8Mo4O24}}$$

Where  $E_{\text{Bi8Mo4O24}}$ ,  $E_{\text{Bi8Mo4O23}}$  were the total energy of Bi<sub>8</sub>Mo<sub>4</sub>O<sub>24</sub> and Bi<sub>8</sub>Mo<sub>4</sub>O<sub>23</sub>, respectively.  $\mu_{\text{O}}$  was half of the total energy of oxygen molecule.

## 3. Results and discussion

### 3.1. Structure and morphology characterization

The crystalline nature and purity of as-prepared pure BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO composites were measured by XRD. As shown in Fig. 1a, all the identifiable diffraction peaks of BMO can be well indexed to the orthorhombic crystal structure (JCPDS card No.76-2388) and no other impurities can be detected, indicating that the calcination and impregnation processes did not markedly change the crystal structure of BMO. Compared to the pure BMO, the position of characteristic peaks of F/BMO-SOVs and F/BMO did not change, which indicates that the Fe(III) clusters were dispersed on the surface of pure BMO and BMO-SOVs instead of getting into its interlayers. Meanwhile, no diffraction peaks of Fe(III) species were detected, this was attributed to the low content and high dispersion of Fe(III) ions in the pure BMO and BMO-SOVs crystal structure. As shown in Fig. 1b, a slight shift of the (131) diffraction peak could be found in the enlarged XRD patterns after the calcination process due to high temperature-induced lattice contraction [32]. The XRD patterns of the other F/BMO-SOVs (5%, 10%, 20%, 25%) samples are similar to that of 15% F/BMO-SOVs (Fig. S1a). The corresponding lattice parameters and cell volumes of samples are listed in Table S1. It is noted that the cell volumes of BMO-SOVs, F/BMO-SOVs, and F/BMO samples slightly decreased in comparison with that of BMO.

The chemical compositions and surface electronic states of as-prepared BMO, BMO-SOVs, and F/BMO-SOVs composites were investigated by XPS. The full XPS survey spectrum is presented in Fig. S1b. It can be seen that the Bi, O, Mo, and Fe elements could all be clearly detected with strong characteristic peaks. Fig. 1c and d display the high-resolution Bi 4f and O 1s XPS spectra of the BMO samples. In the Bi 4f spectra, two asymmetric peaks located at 159.3 and 164.6 eV can be ascribed to Bi 4f<sub>7/2</sub> and Bi 4f<sub>5/2</sub>, respectively, suggesting that the Bi is in the form of Bi<sup>3+</sup> [37]. The corresponding peaks in the spectra of BMO-SOVs and F/BMO-SOVs shifted to 159.5 and 164.8 eV, respectively, being 0.2 eV higher than those of Bi<sub>2</sub>MoO<sub>6</sub>, thus implies the existence of SOVs on the surface of BMO-SOVs and F/BMO-SOVs. However, the Mo 3d spectra of samples BMO, BMO-SOVs, and F/BMO-SOVs are almost identical (Fig. S1c). It can be seen that two characteristic peaks of Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> from Mo<sup>6+</sup> respectively centered at 232.5 and 235.6 eV are observed [38]. As shown in Fig. 1d, the O 1s peak can be deconvoluted into three peaks at 529.8, 530.6, and 531.9 eV, which are ascribed to the Bi-O, Mo-O, and OH group on the surface of Bi<sub>2</sub>MoO<sub>6</sub>, respectively [39]. The O 1s XPS spectra of BMO-SOVs and F/BMO-SOVs shifted to a higher binding energy from



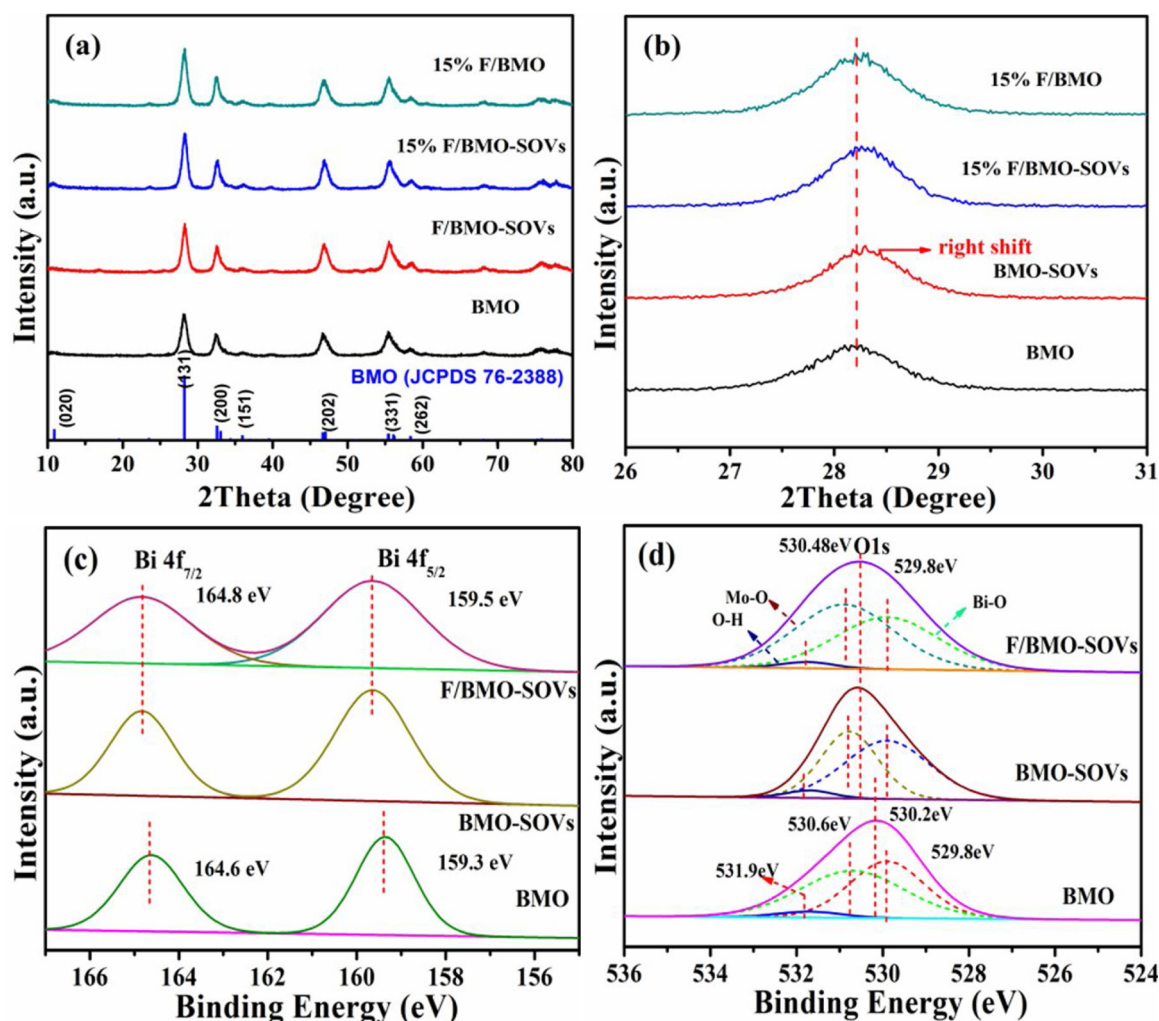


Fig. 1. (a) XRD patterns of samples BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO, (b) Enlarged XRD patterns in a 2θ range of 26–31°, (c) XPS spectra of Bi 4f, and (d) XPS spectra of O 1s for samples BMO, BMO-SOVs, and F/BMO-SOVs.

530.20 eV to 530.48 eV (Fig. 1d), which are attributed to the formation of neighboring oxygen vacancies with a high electron-attracting effect [40]. As presented in Fig. S1d, for the Fe 2p XPS spectrum, two peaks at around 711.0 and 724.7 eV, corresponding to Fe(III) ions in amorphous Fe<sub>2</sub>O<sub>3</sub> and FeOOH, are observed, and can be assigned to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>, respectively [41–43]. These findings clearly corroborate the composition of the obtained F/BMO-SOVs composites and the existence of oxygen vacancies. Moreover, XPS surface elemental analysis was performed to further confirm the existence of oxygen vacancies (Table S2).

The morphology and microstructure of the as-prepared BMO and F/BMO-SOVs were directly investigated by SEM, TEM, and HRTEM. Fig. 2a and b show that the pure BMO sample consists of a large amount of nanosheets with a thickness of 20–50 nm. These nanosheets aggregated together to form hierarchical microspheres with average diameter of 1–2 μm. Furthermore, the morphology of F/BMO-SOVs samples (Fig. 2c and d) are quite similar to the BMO sample, indicating that the calcination processes and Fe(III) clusters grafting does not change the morphological structure of BMO. However, some small spherical Fe(III) clusters are observed on the surface of the BMO hierarchical microspheres (inset of Fig. 2d), indicating a high dispersion of Fe(III) clusters. This observation is in good agreement with the XPS results. Furthermore, the corresponding EDS mapping images (Fig. 3a–d) clearly demonstrated the distribution of Bi, Mo, O, and Fe elements, which gives a strong evidence that the Fe(III) clusters are uniformly

distributed on the surface of BMO-SOVs.

TEM and HRTEM analysis were performed to further elucidate the morphologies and microstructures of BMO and F/BMO-SOVs. Fig. 4a and c show the TEM images of BMO and F/BMO-SOVs, which displayed a flower-like microsphere structure. The HR-TEM images of BMO are shown in Fig. 4b. The lattice spacing is measured to be 0.315 nm, which corresponds to the (131) crystal plane of BMO (inset of Fig. 4b) [44]. High-resolution TEM image shown in Fig. 4d clearly indicates that the Fe(III) clusters were located on the surface of BMO-SOVs. Note that some amorphous clusters can be observed on the surface, which can be indexed as Fe(III) containing clusters. This kind of clusters have also been observed by HRTEM in Cu(II) and Fe(III)-grafted TiO<sub>2</sub> [23–26].

### 3.2. Formation of surface oxygen vacancy

As shown in Fig. 5a and b, the HRTEM image clearly reveals that both BMO and BMO-SOVs are structurally uniform. However, pure BMO sample displays a perfect lattice feature (Fig. 5a), but the edge of lattice fringe for BMO-SOVs becomes blurred and disordered (Fig. 5b), which indicates the surface structure is damaged and SOVs are formed [19]. Hence, the generation of SOVs stems from the calcination process.

To further confirm the existence of oxygen vacancies, EPR spectra analysis was performed. It can be used to directly and accurately detect the existence of oxygen vacancies in semiconductors [45]. The EPR signal curves of BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO are fitted

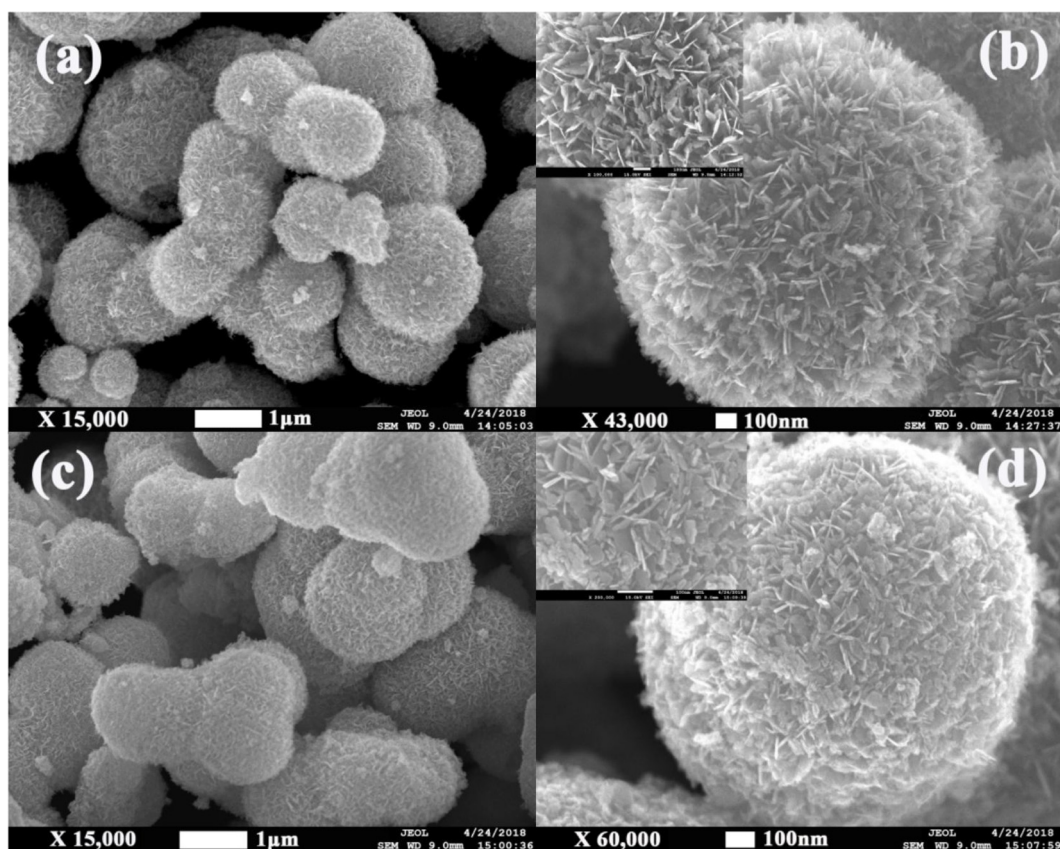


Fig. 2. FE-SEM images of as-prepared BMO (a, b), and F/BMO-SOVs composites (c, d).

and shown in Fig. 5c. It can be seen that the characteristic EPR signal with a small g-value of 1.991 was observed for BMO and F/BMO, which may be attributed to the presence of oxygen vacancies [32]. Compared to BMO and F/BMO, remarkable symmetric peaks with a g-value of

around 2.004 for BMO-SOVs and F/BMO-SOVs were observed, which are typical peaks of surface oxygen vacancies [46,47]. In addition, the intensity of EPR signal for F/BMO-SOVs is considerably stronger than that of BMO-SOVs, which was gradually enhanced with increasing

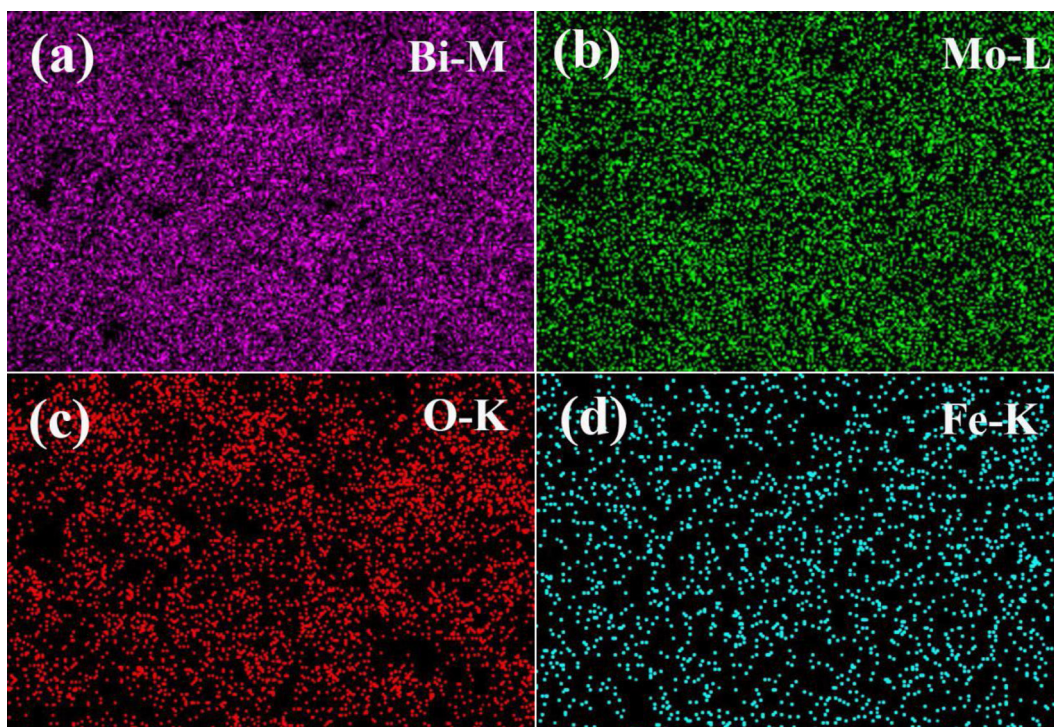


Fig. 3. The corresponding EDS elemental mapping images of (a) Bi, (b) Mo, (c) O, and (d) Fe in sample F/BMO-SOVs.



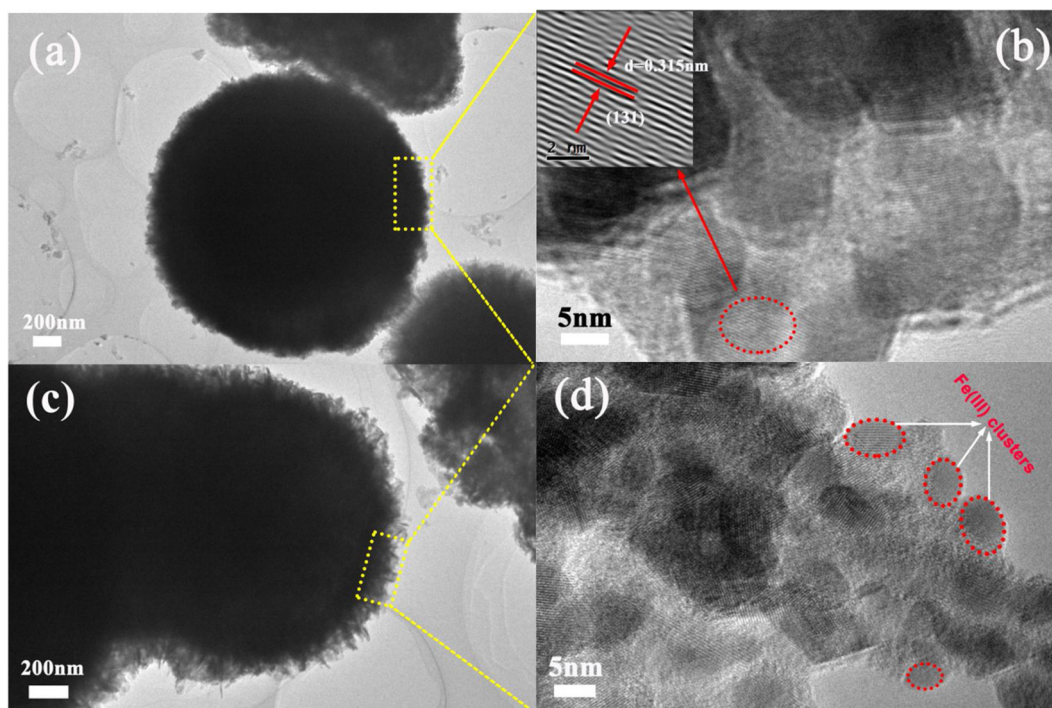


Fig. 4. TEM and HR-TEM images of BMO (a, b), and F/BMO-SOVs composites (c, d).

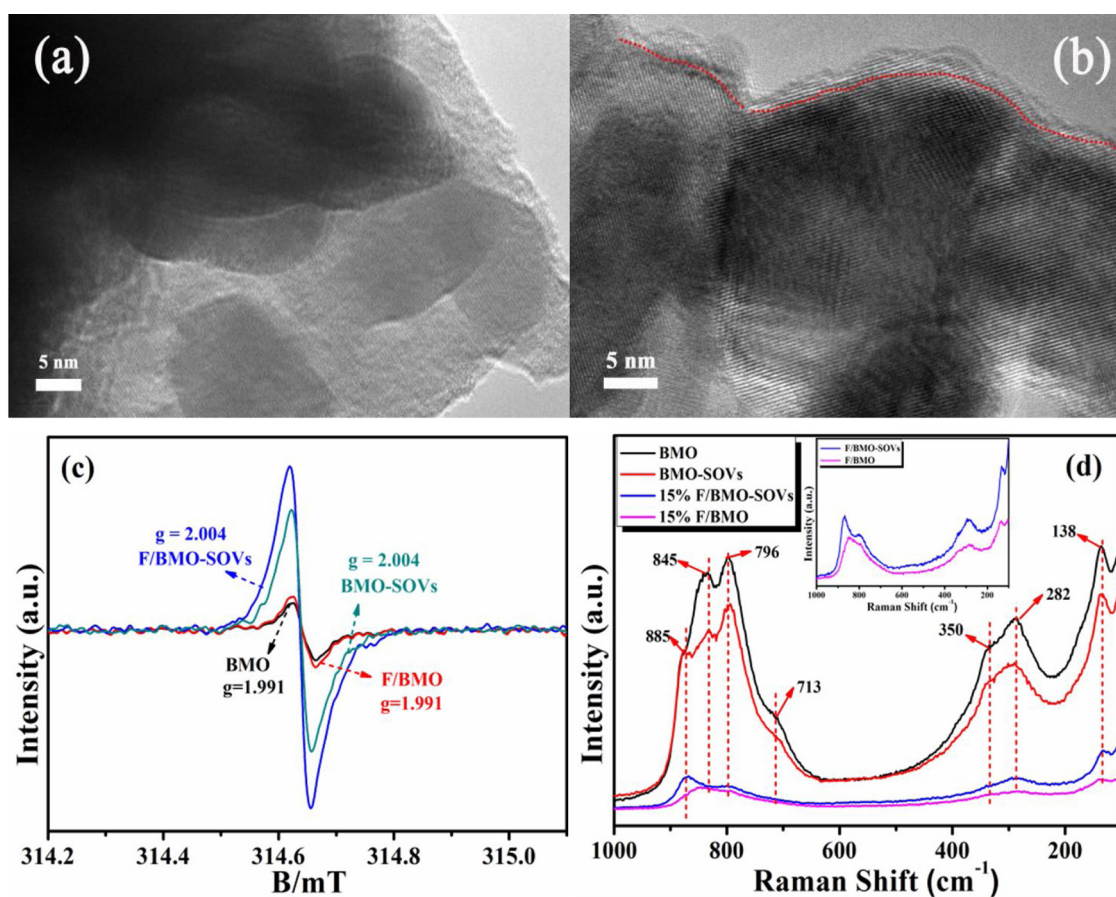
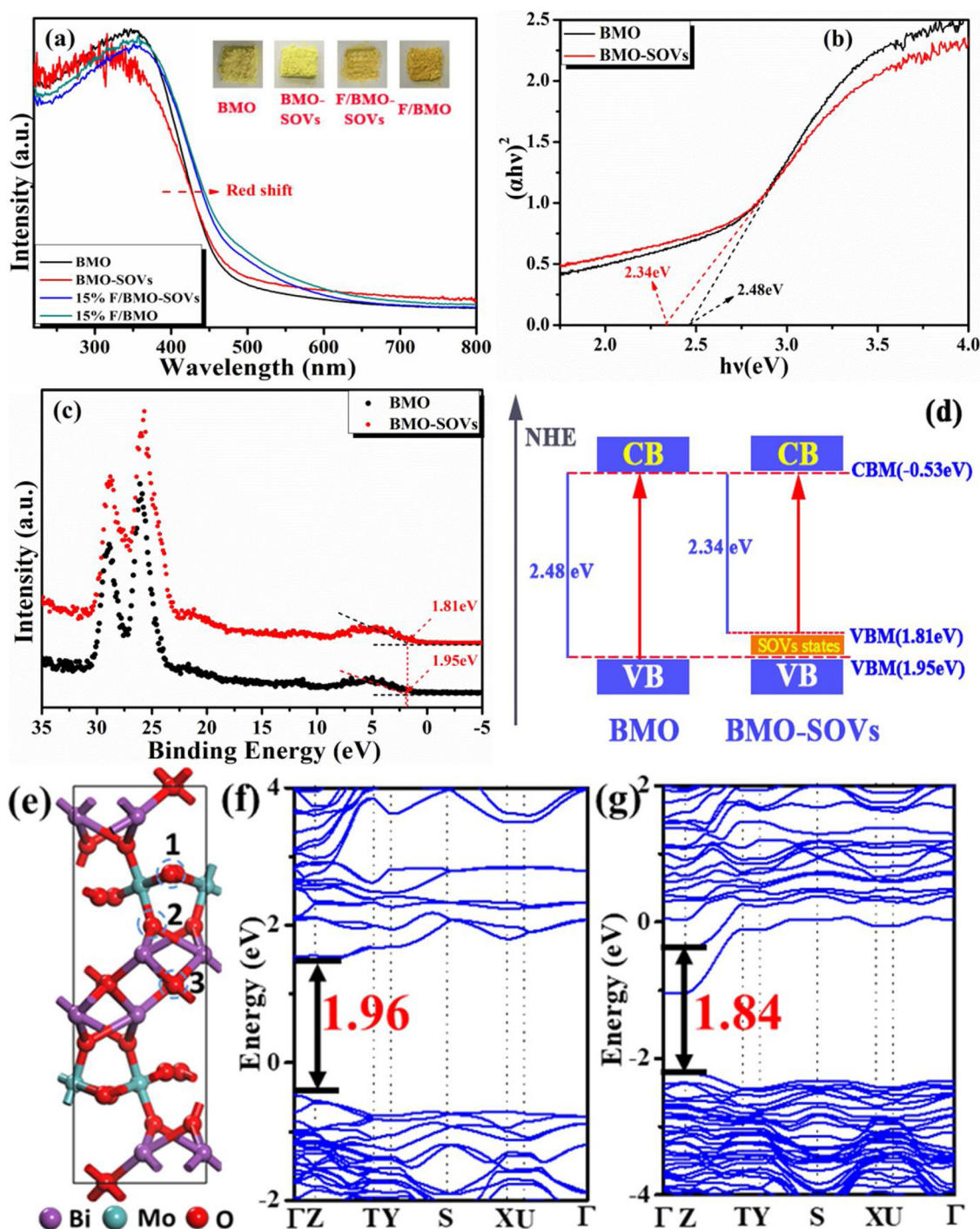


Fig. 5. HR-TEM images of (a) BMO and (b) BMO-SOVs; (c) EPR spectra of BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO at 77 K; (d) Raman spectra of BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO.



**Fig. 6.** (a) UV-vis diffuse reflectance spectra of BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO (inset: the color of the photocatalysts), (b) The band gap value, estimated by a related curve of  $(\alpha h\nu)^2$  versus photon energy plotted, (c) Valence band XPS spectra, and (d) Schematic illustration of BMO and BMO-SOVs band structure, (e) The optimized configuration and oxygen vacancy sites of BMO (The violet, dark green and red spheres represent Bi, Mo and O atoms, respectively.), (f) Band structures of BMO and BMO-SOVs, (g) The Fermi level is set to zero (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

SOVs' concentration [48]. This result further corroborates that the formation of SOVs on the surface of BMO was successfully produced via the thermal treatment process.

Raman spectroscopy is an effective characterization technique to further investigate the crystal defects and the distortion of crystal structure. As shown in Fig. 5d, all of the samples exhibit the typical vibration mode of  $\text{Bi}_2\text{MoO}_6$ . The Raman vibrations at 600 and 400  $\text{cm}^{-1}$  are assigned to the stretching modes of the Mo–O bonds and

the rocking, twisting mode in  $\text{Bi}_2\text{MoO}_6$ , respectively [49]. The vibrating peaks of Mo–O bonds for BMO and BMO-SOVs are stronger than those for F/BMO-SOVs and F/BMO, indicating that the BMO and BMO-SOVs contain more  $\text{MoO}_6$  octahedral structures [50]. The F/BMO-SOVs and F/BMO exhibits a small peak at 885  $\text{cm}^{-1}$ , which is attributed to the vibration of Mo–O bonds in  $\text{MoO}_6$  [51]. The decrease in the intensities of these vibrational modes for the calcined samples suggested the deformation of the crystal structure after calcination, which could be



attributed to the contribution of surface oxygen vacancies [19]. Based on the results from ESR and Raman spectra analyses, the surface oxygen vacancies were successfully produced on the BMO-SOVs and F/BMO-SOVs via the thermal treatment process.

The UV–vis diffuse reflectance spectra of as-prepared BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO are shown in Fig. 6a and Fig. S2. Compared with BMO, the absorption band edge of BMO-SOVs displayed a slight red-shift to visible region and the absorbance is enhanced in the range of 470 to 500 nm, which may be induced by surface oxygen vacancies. However, for F/BMO-SOVs, with an increasing molar ratio of Fe(III) cluster, the light absorption significantly broadens and a red-shift phenomenon occurs. From the inset of Fig. 6a, the color of the as-prepared photocatalysts changes from pale yellow of BMO to deep yellow of BMO-SOVs, indicating the existence of surface oxygen vacancies. In addition, the color of powder changes from deep yellow of BMO-SOVs to pale brown of F/BMO-SOVs, indicating the existence of Fe(III) clusters. The enhanced visible light absorption can be ascribed to the synergistic effect of SOVs and IFCT, as will be discussed in the following.

The band gap energy ( $E_g$ ) of the semiconductors is calculated from the Kubelka-Munk equation as given below [52]:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

where  $\alpha$ ,  $h\nu$ ,  $E_g$ , and  $A$  are the optical absorption coefficient, photonic energy, band gap, and proportionality constant, respectively. The value of  $n$  is 1 for BMO, determined by a direct transition occurring in the semiconductor [53]. Therefore, from the plots of  $(\alpha h\nu)^2$  versus energy ( $h\nu$ ) in Fig. 6b, the  $E_g$  values of BMO and BMO-SOVs can be calculated to be 2.48 and 2.34 eV, respectively. The above results can be ascribed to the synergistic effect between SOVs and Fe(III) clusters co-modification and coupling with BMO. The valence band X-ray photoelectron spectra (VB-XPS) were used to investigate the band structure of BMO and BMO-SOVs. According to the VB XPS spectra, the binding energy of the onset edge of BMO and BMO-SOVs are found to be at 1.95 and 1.81 eV vs NHE (Fig. 6c), respectively. Furthermore, both BMO and BMO-SOVs exhibit the same conduction band (CB) edges, which is calculated to be -0.53 eV based on the equation of  $E_{CB} = E_{VB} - E_g$  [54]. After the secondary thermal treatment, the position of VBM showed a slightly upshift for the BMO-SOVs samples, in which the VBM and CBM positions were 1.81 eV and -0.53 eV, respectively. This result can be ascribed to the introduction of SOVs on BMO could induce generated SOVs states above and partly overlapping of with the valence band (VB) which may be result in the rising of valence band maximum (VBM), thus broadening the VB width and narrowing of the band gap, as previously reported in similar spectra for other hydrogenated and thermal treated photocatalysts [20]. According to the characterization findings, a schematic illustration of the BMO band structure is provided in Fig. 6d.

To determine the position of oxygen vacancy and reveal the effect of oxygen vacancy on the band structure and photocatalytic performances of BMO, density functional theory calculations have been carried, as shown Fig. 6e–g. The oxygen vacancy formation energies of Site-1, Site-2 and Site-3 are 3.45, 3.81 and 3.47 eV, respectively. Therefore, oxygen atom of BMO tends to be removed from Site-1. As shown in Fig. 6f–g, the band gap of BMO is 1.96 eV, while that of BMO-SOVs decreased to 1.84 eV. The differences of band gap between BMO and BMO-SOVs are matched, indicating that band gap of BMO decreases with the appearance of oxygen vacancies. Interestingly, the appearance of impurity state among the band gap in Fig. 6g can greatly improve the photocatalytic ability of BMO-SOVs.

### 3.3. Photocatalytic activity and mechanism

The photocatalytic activities of as-prepared samples were evaluated by degrading phenol under visible light irradiation ( $\lambda \geq 420$  nm).

Fig. 7a and Fig. S3a show the variation of phenol concentration ( $C/C_0$ ) over BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO photocatalysts against reaction time under light irradiation. It was found that all the F/BMO-SOVs samples exhibited much better photocatalytic performances than pure BMO, in which only 4.8% of phenol was degraded. Considering F/BMO-SOVs samples, the 15% F/BMO-SOVs displayed the highest photocatalytic performance in the degradation of phenol compared to BMO, BMO-SOVs, and F/BMO. This result clearly confirms that the SOVs and IFCT effect of Fe(III) clusters act as pivotal roles for the enhanced photocatalytic performance. The optimum Fe(III) loading amount is 15% and further increasing the loading amount of Fe(III) cluster results in a deterioration of activity, which may be ascribed to two reasons. Firstly, the increasing of Fe(III) cluster in the ternary photocatalyst would cause more defects, thus increasing its photocatalytic activity. Secondly, when the amount of Fe(III) clusters added was higher than 15%, the photocatalytic degradation of phenol would gradually decrease, probably due to the formation of recombination sites by excess Fe(III) clusters on the surface of  $\text{Bi}_2\text{MoO}_6$  and the light-shielding effect of Fe(III) cluster.

Furthermore, with increasing irradiation time, the corresponding temporal UV–vis absorption spectra of photodegraded phenol with BMO, BMO-SOVs, and F/BMO-SOVs are monitored and displayed in Fig. 7b. At the beginning of photodegradation of phenol, the characteristic absorption peak is observed at 507 nm. With increasing irradiation time, the absorption peak obviously decreases and virtually no peak could be observed after 180 min irradiation. This clearly demonstrates the complete photocatalytic degradation of phenol by F/BMO-SOVs during the irradiation.

In addition, in order to compare the reaction kinetics of the photodegradation process of phenol quantitatively, the degradation rates were computed using the following pseudo-first-order kinetics Eq. (2) [55]:

$$\ln(C_0/C) = k_{app}t \quad (2)$$

where  $k_{app}$  denotes the apparent rate constant ( $\text{min}^{-1}$ ),  $C_0$  represents the initial phenol concentration ( $\text{mg}\cdot\text{L}^{-1}$ ) and  $C$  represents the final concentration of phenol in solution after irradiation time  $t$  minute. The plot of  $\ln(C_0/C)$  versus irradiation time ( $t$ ), using BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO photocatalysts, is shown in Fig. 7c. The results reveal that the photodegradation of phenol follows pseudo first-order kinetics model. Fig. 7d and Fig. S3b show the apparent rate constants of different samples for photodegradation of phenol. The corresponding calculated rate constants,  $k_{app}$  values are  $1.94 \times 10^{-4}$ ,  $22.4 \times 10^{-4}$ ,  $150.3 \times 10^{-4}$  and  $29.2 \times 10^{-4} \text{ min}^{-1}$ , respectively. It can be deduced that 15% F/BMO-SOVs exhibited the highest photocatalytic activity, which is approximately 77.47 times higher than that of pure BMO. Simulated results of  $k_{app}$  for each process, in the presence of different photocatalysts with regard to phenol, were summarized in Table S3.

The photocatalytic degradation of phenol with different initial dosages of F/BMO-SOVs photocatalyst is shown in Fig. S4. It can be seen that the degradation rate of phenol was improved accordingly, when the amount of F/BMO-SOVs was increased from 0.50 to  $1.25 \text{ g}\cdot\text{L}^{-1}$ , because more active sites would be provided. However, it is important to note that when the amount is more than  $1.50 \text{ g}\cdot\text{L}^{-1}$ , the degradation rate would inversely decrease due to the scattering of light, and would severely reduce the intensity of light penetrating through the phenol solution.

Furthermore, the total organic carbon (TOC) analysis was used to further evaluate the mineralization rate of phenol over BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO under visible light illumination (Fig. 8). It can be observed that only 3%, 21.1%, and 32.2% of TOC were eliminated in the presence of pure BMO, BMO-SOVs, and F/BMO, respectively. In addition, the 15% F/BMO-SOVs displayed the highest TOC mineralization rate for phenol degradation compared to those of BMO, BMO-SOVs, and F/BMO. It can be seen that the F/BMO-SOVs



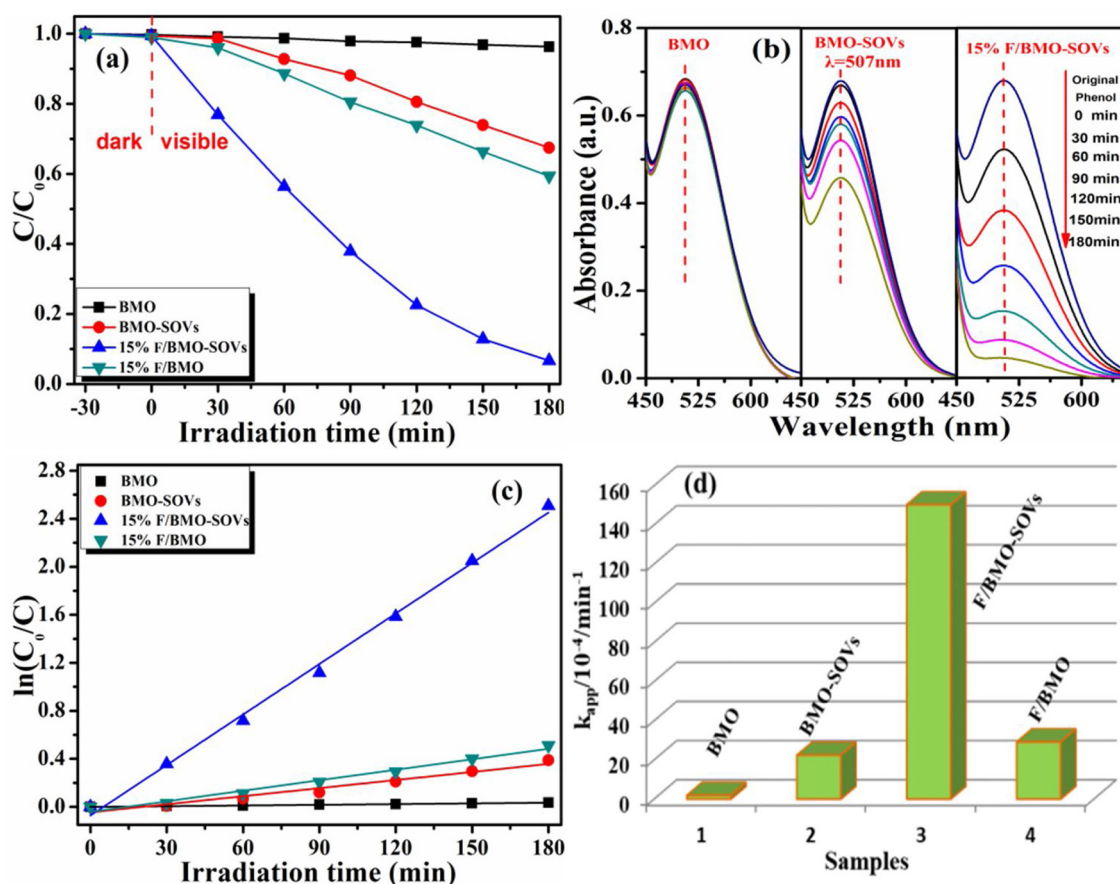


Fig. 7. (a) Photocatalytic degradation efficiency of phenol by BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO, (b) The absorption spectra of phenol during photodegradation under visible light using BMO, BMO-SOVs, and F/BMO-SOVs, respectively, (c) Kinetic plots of  $C/C_0$  versus irradiation time for the photodegradation of phenol with different catalysts, (d) The photodegradation rate constants of phenol using different catalysts.

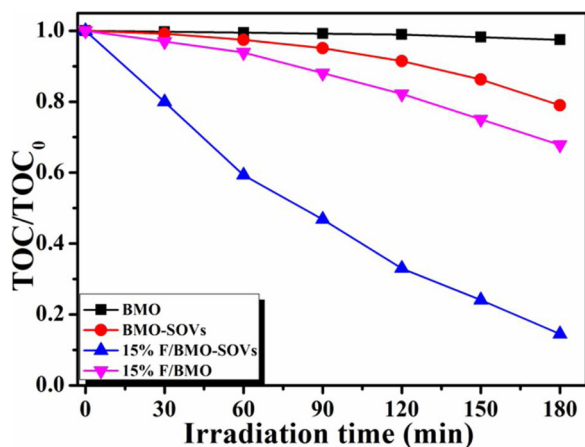


Fig. 8. TOC removal of phenol over BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO composites under visible light illumination.

achieved about 85.6% TOC removal efficiency within 180 min of reaction. This observation is also in accordance with the decolorization result as shown in Fig. 7. The TOC result of 15% F/BMO-SOVs indicates that a significant amount of phenol (85.6%) was mineralized in the photocatalytic process, which is important for practical applications of photocatalysts to avoid secondary pollution.

The practical stability of the optimized F/BMO-SOVs (15%) sample was investigated during five successive photocatalytic degradation experiments as shown in Fig. S5a. The photocatalytic performance shows a slight decrease after five cycles. Fig. S5b shows the XRD patterns of F/

BMO-SOVs samples before and after photodegradation of phenol. It was found that the crystal structure of the F/BMO-SOVs photocatalyst showed no obvious changes during the photocatalytic reaction. Consequently, the F/BMO-SOVs composite is a very stable and reusable photocatalyst, which can be utilized to degrade organic pollutants during practical applications.

PL emission has been widely used to investigate the generation, transfer, and recombination of photogenerated electron-hole pairs [31]. A low PL intensity implies a low recombination rate of free charge carriers. Fig. 9a shows the room-temperature PL spectra of the BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO. It is clear that the PL peak intensity of BMO-SOVs is obviously lower than that of BMO, revealing the role of surface oxygen vacancies in the recombination of photogenerated charge carriers [32]. More importantly, Fe(III) clusters grafted BMO-SOVs shows the weakest photoluminescence emission intensity compared to those of BMO-SOVs and F/BMO, clearly indicating that the synergistic effect of SOVs and IFCT highly promotes efficient electron and hole separation and suppresses their recombination rate, which was further confirmed by time-resolved fluorescence decay spectra (Fig. 9b).

We performed time-resolved photoluminescence experiments to further investigate the recombination process of photogenerated electron-hole pairs in BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO. These spectra are in good agreement with the two-exponential decay models (Fig. 9b). The corresponding lifetimes and intensities are also listed in Table S4. For F/BMO-SOVs sample, the two derived lifetimes  $\tau_1$  and  $\tau_2$  are 0.26 and 2.58 ns with the intensities of 82.7 and 17.3% of the total fluorescence intensity, respectively. The prolonged lifetime is attributed to the synergistic effect the SOVs and the grafted Fe(III) clusters, which

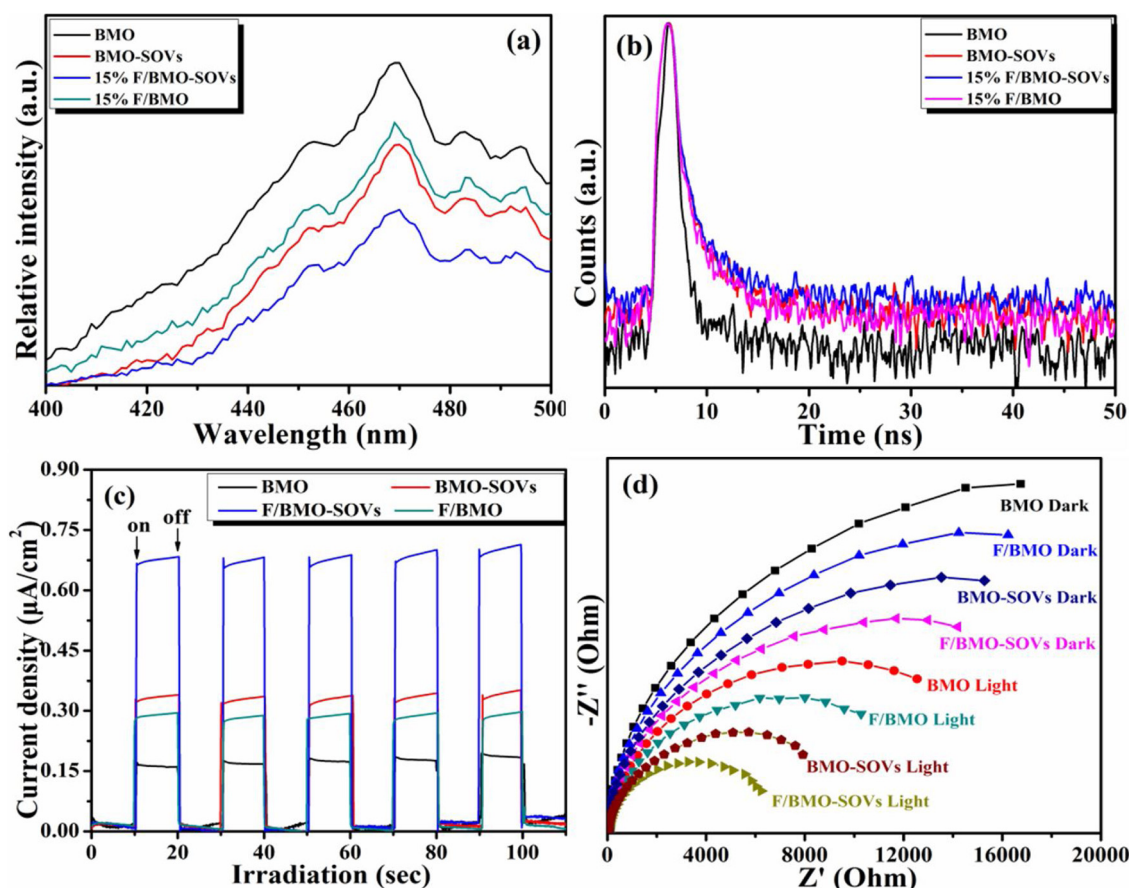


Fig. 9. (a) Photoluminescence spectra, (b) Time-resolved fluorescence decay spectra, (c) Transient photocurrent response under visible light irradiation, and (d) Electrochemical impedance spectroscopy (EIS) of BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO.

effectively inhibit the recombination of photogenerated electron/hole pairs. The results are in accordance with the observations from the PL measurements.

Subsequently, in order to give further evidence to confirm the separation efficiency of photogenerated charge carriers in the samples, the photocurrent generation and EIS experiments were carried out, as shown in Fig. 9c and d. The transient photocurrent responses of BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO, with several on-off cycles of visible light illumination, are displayed in Fig. 9c. It could be seen that 15% F/BMO-SOVs composite exhibits the highest photocurrent intensity, which is about 4.3 times stronger than that of BMO. The increase in photocurrent is attributed to the synergism of SOVs and Fe(III) clusters on BMO, which can efficiently transport photoinduced charge carriers, suppress recombination of photogenerated electrons and holes, and further confirms that the synergism system is far superior to those of BMO, BMO-SOVs, and F/BMO. The typical EIS Nyquist plots of the BMO, BMO-SOVs, F/BMO-SOVs, and F/BMO are provided in Fig. 9d. It is clear that the diameter of the arc radius of F/BMO-SOVs is smaller compared to other photocatalysts, implying that it possesses a stronger ability in the separation and transfer of photogenerated electron-hole pairs. Generally, the smaller radius of the arc reflects the higher efficiency of charge transfer [56]. This result further corroborates that the synergistic effect of SOVs and Fe(III) clusters on BMO can effectively enhance the separation and transfer of photogenerated electron-hole pairs, and improve the photocatalytic activity. This result is well consistent with PL, TR-PL, and photocurrent experiments.

To further understand the underlying photocatalytic mechanism, active species trapping experiments were conducted. In general, benzoquinone (BQ), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), and isopropanol (IPA) were used as the scavengers of superoxide

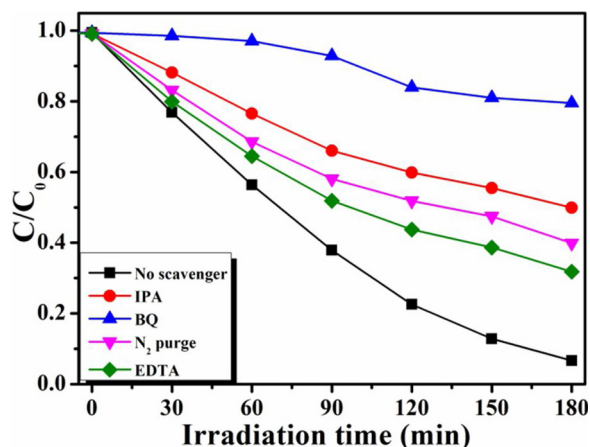


Fig. 10. Comparison of the effect of different radical scavengers during photocatalytic degradation of phenol with 15% F/BMO-SOVs composite under visible light irradiation ( $\lambda \geq 420$  nm).

radicals ( $\cdot\text{O}_2^-$ ), holes ( $\text{h}^+$ ), and hydroxyl radicals ( $\cdot\text{OH}$ ), respectively [32]. The active species trapping experiments in photocatalytic degradation of phenol with 15% F/BMO-SOVs are provided in Fig. 10. The trapping experiments indicate that EDTA-2Na slightly hindered the photocatalytic activity, while the addition of BQ and IPA largely suppressed the photocatalytic degradation efficiency of phenol. In addition, it was observed that only 60.02% of phenol was degraded when  $\text{N}_2$  was conducted to reduce the dissolved  $\text{O}_2$  in the solution, revealing that dissolved  $\text{O}_2$  is key to the photocatalytic degradation of phenol. Thus, it could be inferred that  $\cdot\text{O}_2^-$ ,  $\cdot\text{OH}$ - and  $\text{h}^+$  all participated in the phenol



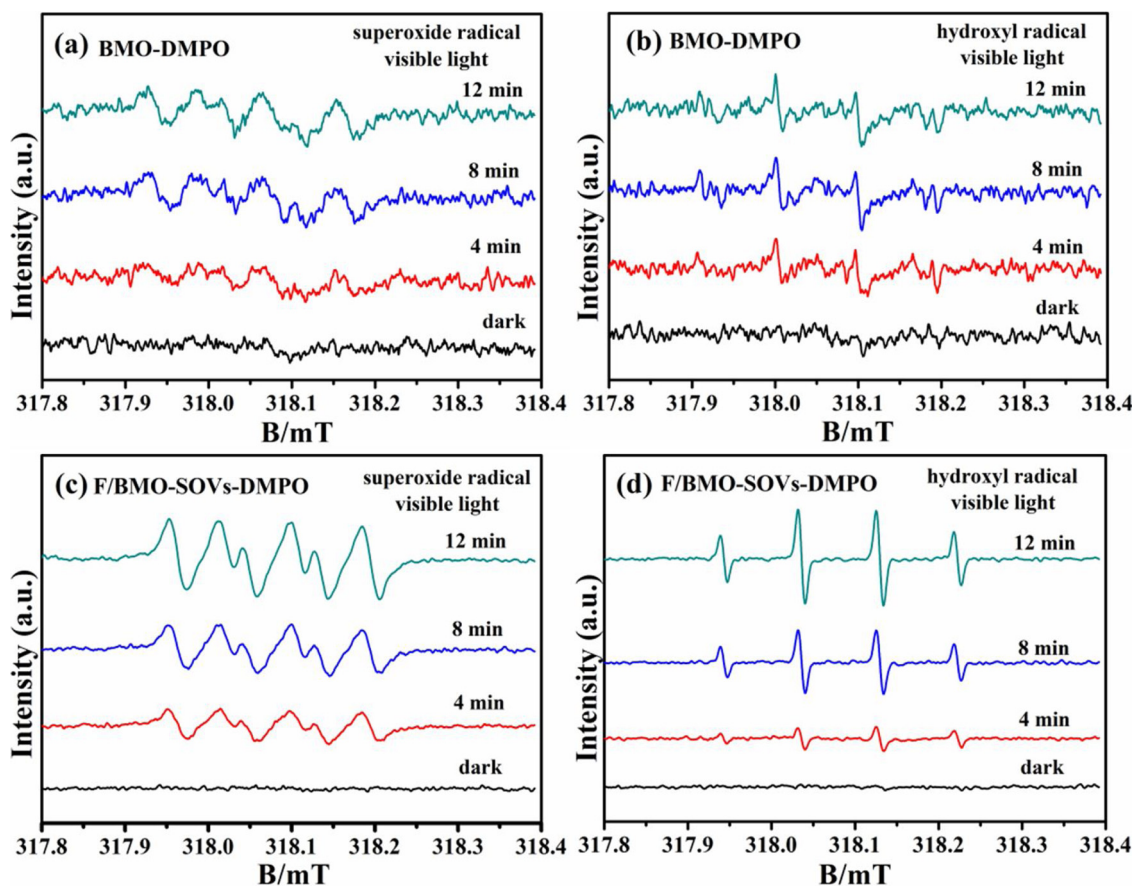


Fig. 11. DMPO spin-trapping ESR spectra of (a) BMO and (c) 15% F/BMO-SOVs in methanol dispersion for  $\text{DMPO} \cdot \text{O}_2^-$ . DMPO spin-trapping ESR spectra of (b) BMO and (d) 15% F/BMO-SOVs in aqueous dispersion for  $\text{DMPO} \cdot \text{OH}$ .

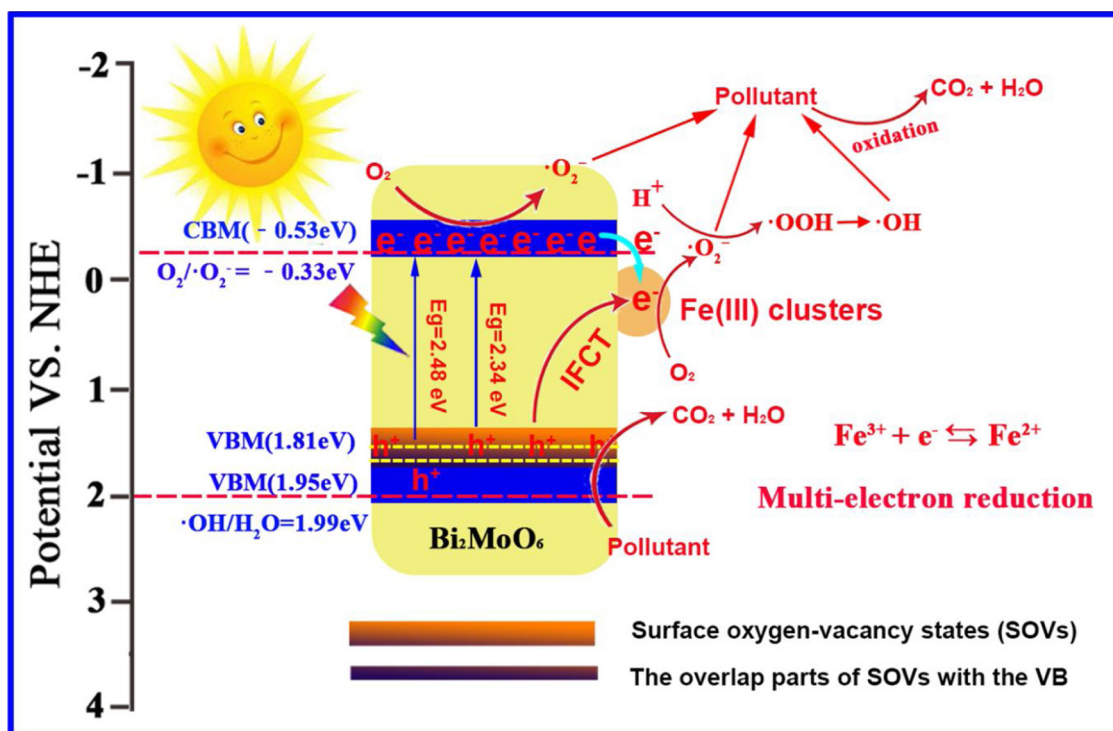
photodegradation process over F/BMO-SOVs, while the  $\cdot\text{O}_2^-$  species are the dominant radicals for photocatalytic degradation of phenol.

To further validate the reactive species and the mechanism accounting for the photocatalytic degradation of phenol, the spin-trapping ESR technique was carried out. Fig. 11 and Fig. S6 shows the results of BMO, BMO-SOVs, and F/BMO-SOVs. It can be seen that the characteristic ESR signal of  $\text{DMPO} \cdot \text{O}_2^-$  adduct and  $\text{DMPO} \cdot \text{OH}$  adduct were not detectable without light irradiation. Under visible light irradiation, the  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  radicals signals were observed. As shown in Fig. 11a and b, the  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  radicals signals is very weak in BMO, indicating that the  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  barely generates in the photocatalysis process. However, for F/BMO-SOVs, the intensity of the peaks increased as the irradiation time is prolonged (Fig. 11c and d). After visible light irradiation for 12 min, we clearly observed the special spectrum with relative intensities of 1 : 1 : 1 : 1 quartet signal, which was considered to be characteristic of  $\text{DMPO} \cdot \text{O}_2^-$  adduct [57]. Meanwhile, a four-line ESR signal with relative intensities of 1 : 2 : 2 : 1 was also obtained, corresponding to the assignment of  $\text{DMPO} \cdot \text{OH}$  adduct [58,59]. The ESR results indicate that  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  radicals are both produced in the photodegradation process over 15% F/BMO-SOVs, which are consistent with the above active species trapping experimental results. Fig. S6 shows the  $\text{DMPO} \cdot \text{O}_2^-$  and  $\text{DMPO} \cdot \text{OH}$  characteristic peaks of BMO-SOVs and F/BMO. Samples BMO-SOVs and F/BMO show a highly intensive  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  radicals signals compared to those of BMO under visible light irradiation.

Based on the above semiconductor band structure analysis and the ESR results, herein, a synergetic mechanism of the electron-hole separation is proposed for SOVs and Fe(III) clusters on BMO, involving an IFCT process for the enhanced photocatalytic degradation of phenol under visible light (Scheme 2). It has been demonstrated that SOV is a

shallow defect, which may be near the conduction band minimum (CBM) or above the valence band maximum (VBM) [60]. As reported by Zhao and co-authors, the band gap of the  $\text{PO}_4$  salt  $\text{LiTi}_2(\text{PO}_4)_3$  significantly reduced due to the formation of oxygen-vacancy states above the VB, under poor oxygen conditions [61]. A similar phenomenon has also been observed on  $\text{BiPO}_4$ ,  $\text{BiFeO}_3$ , and  $\text{Bi}_2\text{WO}_6$  [19,20,40,60]. Furthermore, the present experiments also showed that the photo-responsive wavelength range of BMO-SOVs is extended from 470 nm to about 505 nm (Fig. 6a), which may be attributed to the shallow SOVs states above and partly overlapping with the VBM of BMO, thus broadening the VB width and narrowing of the band gap. The narrowed band gap can led to an enhanced light absorption capability and would thus promoted the efficient separation of photogenerated electron-hole pairs and transfer, then leading to a dramatically enhanced photocatalytic activity [32]. In addition, the introduction of SOV only caused a slight increase of the VBM and a small narrowing of band gap for BMO and hardly any other change of the energy band structure (Fig. 6). Furthermore, when Fe(III) clusters were grafted on the surface of BMO-SOVs, the resulting F/BMO-SOVs photocatalyst showed a very high photocatalytic activity via a synergetic effect of SOVs and Fe(III) clusters. Consequently, the enhanced photocatalytic activity for phenol degradation with F/BMO-SOVs could be explained as follows.

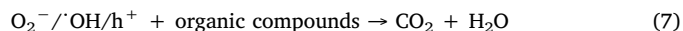
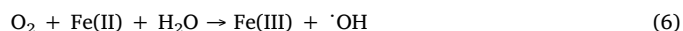
Under visible light irradiation, the photo-excited electrons generated from BMO-SOVs would be divided into two parts (Eq. (3)). One part could transfer into the conduction band of BMO-SOVs. The potential for  $\text{e}^-$  (-0.53 eV vs. NHE) is more negative than  $E(\text{O}_2/\cdot\text{O}_2^-)$  (-0.33 eV vs NHE, pH = 7), which could combine with the dissolved oxygen molecules ( $\text{O}_2$ ) from the environment to generate  $\cdot\text{O}_2^-$  radicals (Eq. (4)). It needs to be noted that a small fraction of electrons in the CB of BMO-SOVs can easily transfer to the Fe(III) clusters owing to a more



**Scheme 2.** Schematic diagram illustrating the proposed degradation mechanism of organic pollutants over 15% F/BMO-SOVs photocatalysts under visible light irradiation ( $\lambda \geq 420$  nm).

positive potential of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  (0.77 eV, vs. SHE) than CB of BMO-SOVs (-0.53 eV, vs. SHE). Another part of the photo-generated electrons can directly transfer from the VB of BMO-SOVs to the  $\text{Fe(III)}$  clusters through the IFCT process. Meanwhile, the  $\text{Fe(III)}$  clusters are reduced to  $\text{Fe(II)}$  after accepting a photogenerated electron ( $\text{Fe(III)} + e^- = \text{Fe(II)}$ ) (Eq. (5)) [25,62]. It is well known that the  $\text{Fe(II)}$  ions are unstable and easily converts back to  $\text{Fe(III)}$  via a multi-electron redox process of  $\text{Fe(II)}$  ( $\text{Fe(II)} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe(III)} + \cdot\text{OH}$ ) [63], which was also found on other cocatalysts [64]. Thus, the  $\text{Fe(III)}$  cluster provides a multi-electron redox center for oxygen reduction and  $\text{Fe(III)}/\text{Fe(II)}$  keeps a dynamic equilibrium, thereby returning to the initial states [41]. Simultaneously, the holes in the VB of BMO-SOVs quickly migrate to its surface and react with the phenol molecules, which is partially responsible for phenol oxidation.

According to the above active species trapping experiments and EPR analysis,  $\cdot\text{OH}$  is the main active species and is playing key roles during the photocatalytic degradation of phenol. However, the photo-induced hole ( $h^+$ ) of BMO-SOVs (1.95 eV vs. NHE) is lower than  $\cdot\text{OH}/\text{OH}^-$  (1.99 eV vs. NHE, pH = 7) [65], thus the holes cannot directly oxidize  $\text{OH}^-$  or  $\text{H}_2\text{O}$  molecules to form  $\cdot\text{OH}$  radicals, which demonstrates that  $\cdot\text{OH}$  are not likely to be generated by the reaction. There is only one explanation that the photogenerated electrons were transferred to the  $\text{Fe(III)}$  clusters through the IFCT process and react with dissolved  $\text{O}_2$  to generate  $\cdot\text{O}_2^-$  radicals. Lately, the yield of  $\cdot\text{OH}$  from  $\cdot\text{O}_2^-$  with the assistance of photoinduced electrons has been revealed (Eq. (6)) [66,67]. The photocatalytic mineralization of phenol involves total transformation into  $\text{CO}_2$  which is confirmed by TOC results in Fig. 8 (Eq. (7)). Therefore, with F/BMO-SOVs catalyst, dual synergism of SOVs and grafted  $\text{Fe(III)}$  clusters greatly reduces the probability of photoinduced electron-hole recombination and shortens the electrons transmission distance, thus leading to a dramatically enhanced photocatalytic activity. Consequently, the change in  $k_{app}$  can also reflect their contribution in dual synergism. The possible reactions are described as follows:



#### 4. Conclusions

In summary, a novel F/BMO-SOVs has been rationally designed and successfully fabricated via a reliable calcination-impregnation process. The 15% F/BMO-SOVs showed the optimal efficiency of phenol degradation, reaching ca. 93.5% within 180 min under visible light irradiation, and the degradation rate constant was determined as nearly 80 time high as that of pure BMO. These results were further demonstrated by 85.6% TOC removal efficiency. The dramatically enhanced photocatalytic activity is reasonably attributed to the synergistic effect between the SOVs,  $\text{Fe(III)}$  clusters and BMO. This heterojunction not only improves the visible light absorption, but also produces the direct interfacial charge transfer (IFCT) from the SOVs isolated states to the surface  $\text{Fe(III)}$  clusters, which significantly promotes the separation and migration of photogenerated electrons and holes, and simultaneously suppresses the recombination of electrons and holes, thus resulting in the high photocatalytic performance on F/BMO-SOVs. In addition, this work not only provides a synergistic effect between SOVs,  $\text{Fe(III)}$  clusters and BMO involving an IFCT process for charge generation and separation, but also provides a new approach to fabricating active photocatalysts for environmental remediation and other applications.

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15JS119).

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.01.056>.

## References

- [1] P. Lisowski, J.C. Colmenares, O. Mašek, W. Lisowski, D. Lisovyt'skiy, A. Kamińska, D. Lomot, ACS Sustainable Chem. Eng. 5 (2017) 6274–6287.
- [2] E. Grabowska, J. Reszczyńska, A. Zaleska, Water Res. 46 (2012) 5453–5471.
- [3] D. Fabbri, A.B. Prevot, E. Pramauro, Appl. Catal. B: Environ. 62 (2006) 21–27.
- [4] A.K.L. Sajjad, S. Shamaia, B. Tian, F. Chen, J. Zhang, Appl. Catal. B: Environ. 91 (2009) 397–405.
- [5] V. Vaianoa, M. Matarangoloa, J.J. Murciab, H. Rojasb, J.A. Navíoc, M.C. Hidalgo, Appl. Catal. B: Environ. 225 (2018) 197–206.
- [6] G.H. Tian, Y.J. Chen, R.T. Zhai, J. Zhou, W. Zhou, R.H. Wang, K. Pan, Ch.G. Tian, H.G. Fu, J. Mater. Chem. A 1 (2013) 6961–6968.
- [7] W. Wei, Y. Dai, B.B. Huang, J. Phys. Chem. C 113 (2009) 5658–5663.
- [8] L.W. Zhang, T.G. Xu, X. Zhao, Y.F. Zhu, Appl. Catal. B: Environ. 98 (2010) 138–146.
- [9] X.X. Chang, T. Wang, P. Zhang, J.J. Zhang, A. Li, J.L. Gong, J. Am. Chem. Soc. 137 (2015) 8356–8359.
- [10] Z. Dai, F. Qin, H.P. Zhao, J. Ding, Y.L. Liu, R. Chen, ACS Catal. 6 (2016) 3180–3192.
- [11] Z.Y. Zhao, Y. Zhou, F. Wang, K.H. Zhang, S. Yu, K. Cao, ACS Appl. Mater. Interfaces 7 (2015) 730–737.
- [12] S.J. Tan, Y.F. Ji, Y. Zhao, A.D. Zhao, B. Wang, J.L. Yang, J.G. Hou, J. Am. Chem. Soc. 133 (2011) 2002–2009.
- [13] X.Y. Xiao, J. Jing, L.Z. Zhang, Appl. Catal. B: Environ. 142–143 (2013) 487–493.
- [14] G. Zhang, Z.Y. Hu, M. Sun, Y. Liu, L.M. Liu, H.J. Liu, C.P. Huang, J.H. Qu, J.H. Li, Adv. Funct. Mater. 25 (2015) 3726–3734.
- [15] K. Zhao, L.Z. Zhang, J.J. Wang, Q.X. Li, W.W. He, J.J. Yin, J. Am. Chem. Soc. 135 (2013) 15750–15753.
- [16] H. Hirakawa, M. Hashimoto, Y. Shiraiishi, T. Hirai, J. Am. Chem. Soc. 139 (2017) 10929–10936.
- [17] H. Li, J. Shang, Z.H. Ai, L.Z. Zhang, J. Am. Chem. Soc. 137 (2015) 6393–6399.
- [18] S.C. Wang, P. Chen, Y. Bai, J.H. Yun, G. Liu, L.Z. Wang, Adv. Mater. 30 (2018) 1800486.
- [19] Z. Wei, Y.F. Liu, J. Wang, R.L. Zong, W.Q. Yao, J. Wang, Y.F. Zhu, Nanoscale 7 (2015) 13943–13950.
- [20] D. Chen, F. Niu, L.S. Qin, S. Wang, N. Zhang, Y.X. Huang, Sol. Energy Mater. Sol. Cells 171 (2017) 24–32.
- [21] Y.Q. Wu, G.X. Lu, Phys. Chem. Chem. Phys. 16 (2014) 4165–4175.
- [22] Y. Nosaka, S. Takahashi, H. Sakamoto, A.Y. Nosaka, J. Phys. Chem. C 115 (2011) 21283–21290.
- [23] X.Q. Qiu, M. Miyauchi, K. Sunada, M. Minoshima, M. Liu, Y. Lu, D. Li, Y. Shimodaira, Y. Hosogi, Y. Kuroda, K. Hashimoto, ACS Nano 6 (2012) 1609–1618.
- [24] H.G. Yu, H. Irie, K. Hashimoto, J. Am. Chem. Soc. 132 (2010) 6898–6899.
- [25] M. Liu, X.Q. Qiu, M. Miyauchi, K. Hashimoto, J. Am. Chem. Soc. 135 (2013) 10064–10072.
- [26] M. Liu, R. Inde, M. Nishikawa, X.Q. Qiu, D. Atarashi, E. Sakai, Y. Nosaka, K. Hashimoto, M. Miyauchi, ACS Nano 8 (2014) 7229–7238.
- [27] Q. Liu, T.X. Chen, Y.R. Guo, Z.G. Zhang, X.M. Fang, Appl. Catal. B: Environ. 205 (2017) 173–181.
- [28] H.G. Yu, W.Y. Chen, X.F. Wang, Y. Xu, J.G. Yu, Appl. Catal. B: Environ. 187 (2016) 163–170.
- [29] W.B. Sun, H.Y. Zhang, J. Lin, J. Phys. Chem. C 118 (2014) 17626–17632.
- [30] C.J. Huang, J.L. Hu, S. Cong, Z.G. Zhao, X.Q. Qiu, Appl. Catal. B: Environ. 174–175 (2015) 105–112.
- [31] X. Feng, W.D. Zhang, Y.J. Sun, H.W. Huang, F. Dong, Environ. Sci.: Nano 4 (2017) 604–612.
- [32] D.J. Wang, H.D. Shen, L. Guo, C. Wang, F. Fu, Y.C. Liang, Appl. Surf. Sci. 436 (2018) 536–547.
- [33] Z.H. Yuan, J.H. Jia, L.D. Zhang, Mat. Chem. Phys. 73 (2002) 323–326.
- [34] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558–561.
- [35] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) 1396.
- [36] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188–5192.
- [37] W. Zhao, C. Li, A.J. Wang, C.C. Lv, W.H. Zhu, S.P. Dou, Q. Wang, Q. Zhong, Phys. Chem. Chem. Phys. 19 (2017) 28696–28709.
- [38] J.H. Guo, L. Shi, J.Y. Zhao, Y. Wang, K.B. Tang, W.Q. Zhang, C.Z. Xie, X.Y. Yuan, Appl. Catal. B: Environ. 224 (2018) 692–704.
- [39] Y.S. Xu, W.D. Zhang, Dalton Trans. 42 (2013) 1094–1101.
- [40] Y.H. Lv, W.Q. Yao, R.L. Zong, Y.F. Zhu, Sci. Rep. 6 (2016) 19347.
- [41] H.G. Yu, H. Irie, Y. Shimodaira, Y. Hosogi, Y. Kuroda, M. Miyauchi, K. Hashimoto, J. Phys. Chem. C 11 (2010) 16481–16487.
- [42] H.G. Yu, G.Q. Cao, F. Chen, X.F. Wang, J.G. Yu, M. Lei, Appl. Catal. B: Environ. 160–161 (2014) 658–665.
- [43] S.Q. Liu, P.P. Deng, G.P. Dai, Y. Liang, S.Y. Zhang, Ceram. Int. 42 (2016) 10094–10098.
- [44] Y. Ma, Y.L. Jia, Z.B. Jiao, M. Yang, Y.X. Qi, Y.P. Bi, Chem. Commun. 51 (2015) 6655–6658.
- [45] C. Zhang, Y.F. Zhu, Chem. Mater. 17 (2005) 3537–3545.
- [46] J.G. Hou, S.Y. Cao, Y.Z. Wu, F. Liang, Y.F. Sun, Z.S. Lin, L.C. Sun, Nano Energy 32 (2017) 359–366.
- [47] W.T. Bi, C.M. Ye, C. Xiao, W. Tong, X.D. Zhang, W. Shao, Y. Xie, Small 10 (2014) 2820–2825.
- [48] H. Li, J. Li, Z.H. Ai, F.L. Jia, L.Z. Zhang, Angew. Chem. Int. Ed. 57 (2018) 122–138.
- [49] H.B. Fu, C.S. Pan, W.Q. Yao, Y.F. Zhu, J. Phys. Chem. B 109 (2005) 22432–22439.
- [50] Z.X. Yang, M. Shen, K. Dai, X.H. Zhang, H. Chen, Appl. Surf. Sci. 430 (2018) 505–514.
- [51] R. Murugan, Physica B 352 (2004) 227–232.
- [52] Z. Wan, G.K. Zhang, X.Y. Wu, S. Yin, Appl. Catal. B: Environ. 207 (2017) 17–26.
- [53] D.J. Wang, H.D. Shen, L. Guo, F. Fu, Y.C. Liang, New J. Chem. 40 (2016) 8614–8624.
- [54] Q. Wang, W. Wang, L.L. Zhong, D.M. Liu, X.Z. Cao, F.Y. Cui, Appl. Catal. B: Environ. 220 (2018) 290–302.
- [55] C.W. Tan, G.Q. Zhu, M. Hojamberdiev, K. Okada, J. Liang, X.C. Luo, P. Liu, Appl. Catal. B: Environ. 152–153 (2014) 425–436.
- [56] X.J. Bai, L. Wang, R.L. Zong, Y.H. Lv, Y.Q. Sun, Y.F. Zhu, Langmuir 29 (2013) 3097–3105.
- [57] W.W. He, H.M. Jia, W.G. Wamer, Z. Zheng, P.J. Li, J.H. Callahan, J.J. Yin, J. Catal. 320 (2014) 97–105.
- [58] P.X. Qiu, C.M. Xu, H. Chen, F. Jiang, X. Wang, R.F. Lu, X.R. Zhang, Appl. Catal. B: Environ. 206 (2017) 319–327.
- [59] P.H. Shao, Z.J. Ren, J.Y. Tian, S.S. Gao, X.B. Luo, W.X. Shi, B.Y. Yan, J. Li, F.Y. Cui, Chem. Eng. J. 323 (2017) 64–73.
- [60] Y.H. Lv, Y.Y. Zhu, Y.F. Zhu, J. Phys. Chem. C 117 (2013) 18520–18528.
- [61] L.J. Chen, Y.J. Zhao, J.Y. Luo, Y.Y. Xia, Phys. Lett. A 375 (2011) 934–938.
- [62] M. Nishikawa, Y. Mitani, Y. Nosaka, J. Phys. Chem. C 116 (2012) 14900–14907.
- [63] M. Miyauchi, H. Irie, M. Liu, X.Q. Qiu, H.G. Yu, K. Sunada, K. Hashimoto, J. Phys. Chem. Lett. 7 (2015) 75–84.
- [64] Y. Nosaka, S. Takahashi, Y. Mitani, X. Qiu, M. Miyauchi, Appl. Catal., B: Environ. 111–112 (2012) 636–640.
- [65] X.L. Hu, J. Tian, Y.J. Xue, Y.J. Li, H.Z. Cui, ChemCatChem 9 (2017) 1511–1516.
- [66] S.M. Sun, W.Z. Wang, L. Zhang, L. Zhou, W.Z. Yin, M. Shang, Environ. Sci. Technol. 43 (2009) 2005–2010.
- [67] B. Yuan, C.H. Wang, Y. Qi, X.L. Song, K. Mu, P. Guo, L.T. Meng, H.M. Xi, Colloids and Surfaces A: Physicochem. Eng. Aspects 425 (2013) 99–107.